NEWSBLAST

Singin' the blues

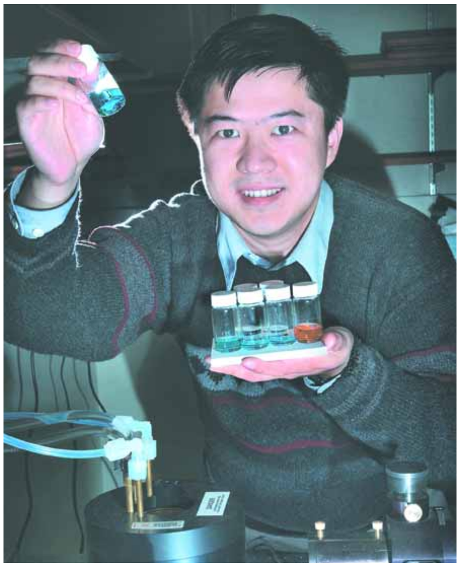
Few mysteries have made chemists sing the blues longer than the nature of those giant molecules, or supramolecular structures, that form in solutions of molybdenum and oxygen.

"The nature of 'molybdenum blue solutions' has remained a fascinating enigma for inorganic chemists since the late 1700s and early 1800s," said Tianbo Liu (ACS '99) of Brookhaven National Laboratory in Upton, NY.

Liu and associates have become the enigma busters.

Using static and dynamic laser light scattering, they deciphered the structure of the big polyoxomolybdate (POM) molecules that form in molybdenum solutions and confer the blue color. The molecules have a chemical formula of Mo_5O_{14}. Unlike table salt and other soluble inorganic compounds, giant POMs do not occur as single ions in water. Rather, POMs cluster together. Scientists did not understand the structures of the aggregates.

"Once we found how big these molecules were [2.5–5.1 nanometers, or billionths of a meter], we realized we could use laser light scattering to decipher the structure," Liu explained. It enabled Liu to determine the radius, size distribution, mass, and other characteristics of the clusters. Liu concluded that individual POM molecules assemble into hollow, spherical structures with an outer surface that resembles a blackberry.


BROOKHAVEN NATIONAL LABORATORY

Tianbo Liu (ACS '99)

The solution to the structural enigma led to another mystery: What's the physics behind the structure? Sodium and chloride ions distribute evenly in a solution to maintain charged neutrality. The charged particles in proteins form large clusters that precipitate from solution. But POM clusters stay in solution.

"We believe we are seeing a new, thermodynamically stable state for solutes, where large-size, single molecules with a limited amount of charge on the surface will all form hollow spherical clusters," Liu said.

He reported that some other giant molecules with different shapes also assume the blackberry structure, further suggesting that it may be a universal state for certain solutes. ⬢

Green dry-cleaning

Liquid carbon dioxide has been the dry-cleaning industry's great hope as a permanent replacement for chlorinated solvents like perchloroethylene, which have potential health and environmental risks.

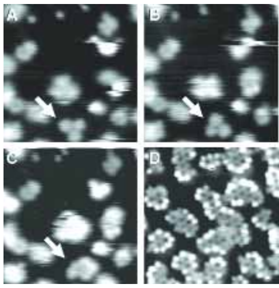
CO_2 avoids those toxicity problems yet works much like traditional dry-cleaning solvents. Thanks to low surface tension and viscosity, it easily penetrates garment fibers and dissolves dirt, grease, and oils in a wide range of fabrics. Nonflammable and odorless, it produces no hazardous waste or emissions that require special equipment. Thousands of dry-cleaning establishments already use CO_2 cleaning fluids, which usually require additives, including surfactants based on compounds of silicon or fluorine, to enhance their dirt-busting power. Imperial Chemical Industries, London, and the Linde Gas Group, Wiesbaden, Germany, reported development of a "revolutionary" dry-cleaning fluid called Washpoint that could expand the use of CO_2. Washpoint contains an additive that greatly enhances CO_2's cleaning power. The firms did not disclose the additive's identity because it is proprietary, or a trade secret.

CO_2 dry-cleaning is a spin-off from the aerospace industry, which years ago developed a supercritical fluid technology to clean high-tech metals and composite materials. Supercritical fluids are at a temperature and pressure greater than or equal to the critical temperature and pressure of the fluid. CO_2's critical pressure is about 1070 pounds per square inch, and its critical temperature is about 31 °C. ⬢

H_2O: The action movie

H_2O gets a lot of press for a simple molecule. Scores of new research papers on water and ice appear annually. Now scientists at the Lawrence Berkeley National Laboratory have produced an action movie starring individual water molecules. It has a surprise ending.

Miquel Salmeron and co-workers put water molecules on a single crystal of palladium and used a special scanning tunneling microscope (STM) to track their motion. As expected, single molecules migrated across the surface to aggregate into clusters of dimers, trimers, tetramers, pentamers, and hexamers.



SCIENCE

Clusters formed by accretion of water molecules

The surprise, they reported in the September 13 edition of *Science*, came from the molecules' motion.

"Isolated water molecules moved by hopping from one lattice point [on the substrate's crystal] to the nearest neighboring point, whereupon if they collided with another water molecule, they began to form clusters," said Salmeron. "The speed with